conductors of electricity is

$$\varepsilon'' \propto \frac{\sigma}{\omega\varepsilon_0} \propto \left(\frac{\omega}{\omega_p}\right)^{n_1-1} + \left(\frac{\omega}{\omega_p}\right)^{n_2-1} \qquad (15.17)$$

where ω is the angular frequency $2\pi f$, ω_p is the hopping frequency of the carriers and n_1, n_2 are constants. Inherent to this equation is the notion that individual polarization events, whether they be the hopping of ions in conductors or the reorientation of dipoles in dielectrics, do not take place independently of each other but, rather, interact cooperatively. This means that if a dipole in a crystal reorients itself, this must influence neighbouring dipoles in the crystal. At this stage, however, it is not clear how Jonscher's Law can be applied quantitatively to the characterization of such phenomena. A further discussion of complex plane diagrams has been given in Chapter 13, in which principal attention is given to conductivity rather than dielectric behaviour.

15.4 Ferroelectricity

Ferroelectric materials are distinguished from ordinary dielectrics by (a) their extremely large permittivities and (b) the possibility of retaining some residual electrical polarization after an applied voltage has been switched off. As the potential difference applied across a dielectric substance is increased, a proportional increase in the induced polarization, P, or stored charge, Q, occurs (equation 15.10). With ferroelectrics, this simple linear relation between P and V does not hold, as shown in Fig. 15.12. Instead, more complicated behaviour with a hysteresis loop is observed. The polarization behaviour that is observed on increasing the voltage is not reproduced on subsequently decreasing the voltage. Ferroelectrics exhibit a saturation polarization, P_s, at high field strength (for $BaTiO_3$, $P_s = 0.26\ C\ m^{-2}$ at 23 °C) and a remanent polarization, P_R, which is the value retained as V is reduced to zero after saturation. In order to reduce the polarization to zero, a reverse field is required; this is the coercive field, E_c.

Some common ferroelectric materials are listed in Table 15.2. All are characterized by structures in which one type of cation present, e.g. Ti^{4+} in $BaTiO_3$, can undergo a significant displacement, e.g. 0.1 Å, relative to its anionic neighbours. These charge displacements give rise to dipoles and the high dielectric constants that are characteristic of ferroelectrics.

The unit cell of $SrTiO_3$, which has the same perovskite structure as $BaTiO_3$, is shown in Fig. 6.15. In the primitive cubic unit cell, titanium ions occupy corner positions, oxygen ions occupy the cube edge centres and strontium is at the cube body centre. Alternatively, the unit cell may be displaced so that its origin is at strontium. In this case, titanium is at the body centre and oxygen ions occupy the face centre positions. Either way, the structure is composed of (TiO_6) octahedra which link together by sharing corners to form a three-dimensional

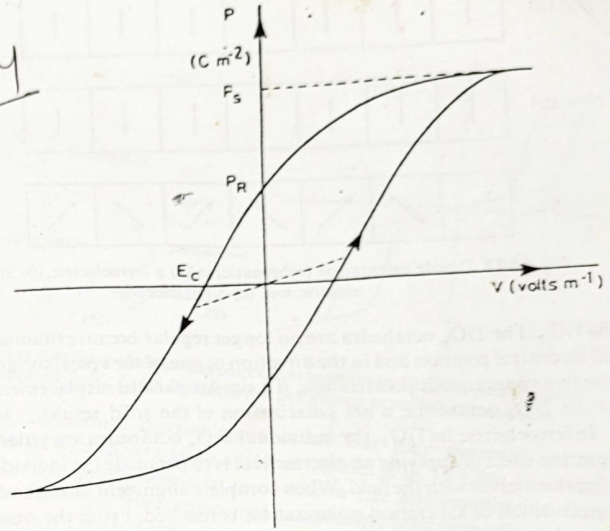


Fig. 15.12 Hysteresis loop of a ferroelectric. The dashed line passing through the origin represents the behaviour of normal dielectric materials

Table 15.2 *Some ferroelectric materials*

	T_c(°C)
Barium titanate, $BaTiO_3$	120
Rochelle salt, $KNaC_4H_4O_6.4H_2O$	Between −18 and +24
Potassium niobate, $KNbO_3$	434
Potassium dihydrogen phosphate, KDP, KH_2PO_4	−150
Lead titanate, $PbTiO_3$	490
Lithium niobate, $LiNbO_3$	1210
Bismuth titanate, $Bi_4Ti_3O_{12}$	675
Gadolinium molybdate, GMO, $Gd_2(MoO_4)_3$	159
Lead zirconate titanate, PZT, $Pb(Zr_xTi_{1-x})O_3$	Depends on x

framework; strontium ions occupy twelve coordinate cavities within this framework.

This ideal, cubic, perovskite structure, which is stable above 120 °C in $BaTiO_3$, does not possess a net dipole moment since the charges are symmetrically positioned. The material therefore behaves as a normal dielectric, albeit with a very high dielectric constant. Below 120 °C, a structural distortion occurs in

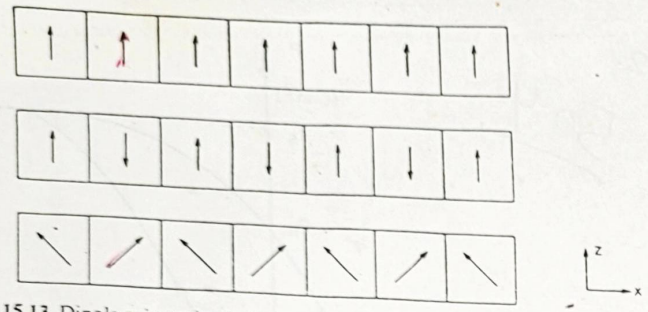


Fig. 15.13 Dipole orientation (schematic) in (a) a ferroelectric, (b) an antiferroelectric and (c) a ferrielectric

$BaTiO_3$. The TiO_6 octahedra are no longer regular because titanium is displaced off its central position and in the direction of one of the apical oxygens. This gives rise to a spontaneous polarization. If a similar parallel displacement occurs in all of the TiO_6 octahedra, a net polarization of the solid results.

In ferroelectric $BaTiO_3$, the individual TiO_6 octahedra are polarized all of the time; the effect of applying an electric field is to persuade the individual dipoles to align themselves with the field. When complete alignment of all the dipoles occurs the condition of saturation polarization is reached. From the observed magnitude of P_s, it has been estimated that titanium is displaced by ~ 0.1 Å off the centre of its octahedron and in the direction of one of the oxygens. This has been confirmed by X-ray crystallography. This distance of 0.1 Å or 10 pm is fairly small when compared with the average Ti—O bond distance of ~ 1.95 Å in TiO_6 octahedra. Alignment of dipoles is shown schematically in Fig. 15.13(a); each arrow represents, for example, one distorted TiO_6 octahedron and all are shown with a common direction of distortion.

In ferroelectrics such as $BaTiO_3$, domain structures form because adjacent TiO_6 dipoles tend to align themselves parallel to each other (Fig. 15.14). The domains are of variable size but are usually quite large, tens or hundreds of angstroms across. Within a single domain, the polarization of the dipoles has a common crystallographic direction. The net polarization of a piece of ferroelectric material is the vector resultant of the polarizations of the individual domains.

Application of an electric field across a ferroelectric leads to a change in the net polarization. This can arise from several possible processes:

(a) The direction of polarization of the domains may change. This would happen if all the TiO_6 dipoles within a domain were to change their orientation, e.g. if all the dipoles in domain (ii) in Fig. 15.14 changed their orientation so as to be parallel to the dipoles in domain (i).
(b) The magnitude of P within each domain may increase, especially if some randomness in dipole orientation is present before the field is applied.

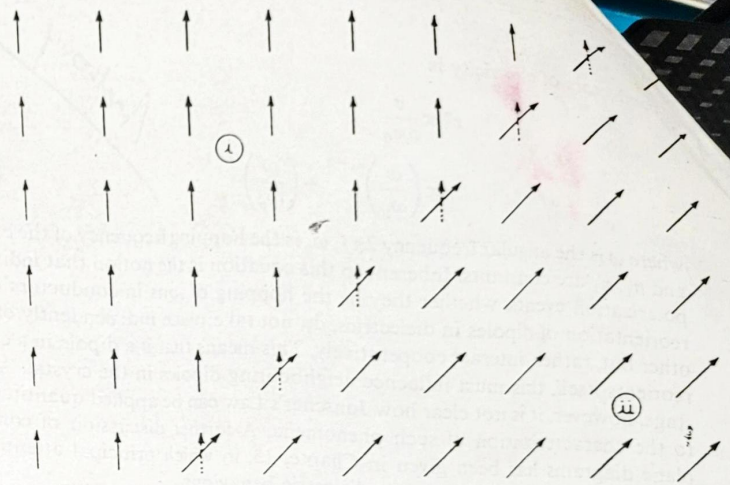


Fig. 15.14 Ferroelectric domains separated by a domain wall or boundary

(c) Domain wall migration may occur such that favourably oriented domains grow in size at the expense of unfavourably oriented ones. For example, domain (i) in Fig. 15.14 may grow by migration of the domain wall one step to the right. To effect this, the dipoles at the edge of domain (ii) change their orientation to the positions shown dashed.

The ferroelectric state is usually a low temperature condition since the effect of increasing thermal motions at high temperatures is sufficient to break down the common displacement in adjacent octahedra and destroy the domain structure. The temperature at which breakdown occurs is the ferroelectric Curie temperature, T_c (Table 15.2). Above T_c, the material is paraelectric (i.e. non-ferroelectric). High dielectric constants still occur above T_c (Fig. 15.15), but no residual polarization is retained in the absence of an applied field. Above T_c, ε' is usually given by the Curie–Weiss Law, $\varepsilon' = C/(T-\theta)$, where C is the Curie constant and θ the Curie–Weiss temperature. Usually, T_c and θ either coincide or differ by only a few degrees. The ferroelectric–paraelectric transition, at T_c, is an example of an order–disorder phase transition. However, unlike order–disorder phenomena in, say, brass, no long range diffusion of ions occurs. Rather, the ordering that occurs below T_c involves preferential distortion or tilting of polyhedra and is therefore an example of a displacive phase transition (Chapter 12). In the high temperature paraelectric phase, the distortions or tilts of the polyhedra, if they occur at all, are randomized.

A necessary condition for a crystal to exhibit spontaneous polarization and be ferroelectric is that its space group should be non-centrosymmetric (Chapter 6). Often the symmetry of the paraelectric phase stable above T_c is centrosymmetric

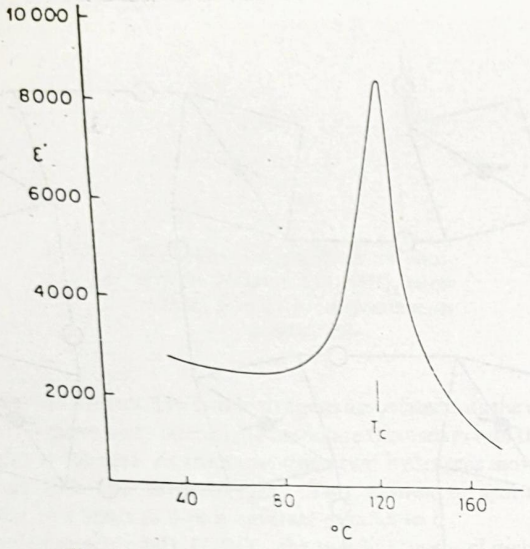


Fig. 15.15 Dielectric constant of $BaTiO_3$ ceramic

and the ordering transition that occurs on cooling simply involves a lowering of symmetry to that of a non-centric space group.

Several hundred ferroelectric materials are now known, including a large number of oxides that have distorted (non-cubic) perovskite structures. These contain cations that are happy in a distorted octahedral environment—Ti, Nb, Ta—and the asymmetric bonding within the MO_6 octahedron gives rise to spontaneous polarization and a dipole moment. Not all perovskites are ferroelectric, e.g. $BaTiO_3$ and $PbTiO_3$ are whereas $CaTiO_3$ is not, and this may be correlated with the ionic radii of the ions involved. It appears that the larger Ba^{2+} ion causes an expansion of the unit cell relative to Ca^{2+}; this results in longer Ti–O bonds in $BaTiO_3$ and allows the Ti^{4+} ions more flexibility to move within the TiO_6 octahedra. Other ferroelectric oxides contain cations that are asymmetrically bonded because of the presence of a lone pair of electrons in their outer valence shell. These are the cations of the heavy *p*-block elements that are in oxidation states two less than the group valency, e.g. Sn^{2+}, Pb^{2+}, Bi^{3+}, etc.

Ferroelectric oxides are used in capacitors because of their high dielectric constants, especially near to T_c (Fig. 15.15). In order to maximize ε', for practical applications, it is therefore necessary to displace the Curie point so that it is close to room temperature. The Curie point of $BaTiO_3$, 120 °C (Fig. 15.15), may be lowered and broadened when either Ba^{2+} or Ti^{4+} are partially replaced by other ions. The substitution $Ba^{2+} \rightleftharpoons Sr^{2+}$ causes a unit cell contraction and reduction in T_c; replacement of 'active' Ti^{4+} by 'non-active' tetravalent ions such as Zr^{4+} and Sn^{4+} causes a rapid decrease in T_c.

A related type of spontaneous polarization occurs in *antiferroelectric* materials. In this, individual dipoles again occur but they generally arrange themselves so as to be antiparallel to adjacent dipoles (Fig. 15.13b). As a result, the net spontaneous polarization is zero. Above the antiferroelectric Curie temperature, the materials revert to normal paraelectric behaviour. Examples of antiferroelectrics, with their Curie temperatures, are: lead zirconate, $PbZrO_3$, 233 °C; sodium niobate, $NaNbO_3$, 638 °C; and ammonium dihydrogen phosphate, $NH_4H_2PO_4$, −125 °C.

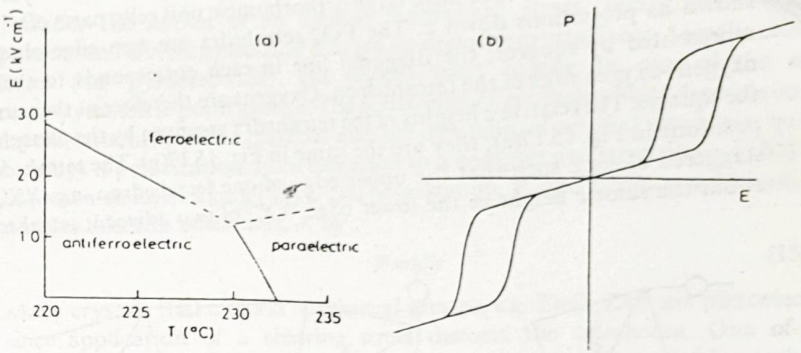


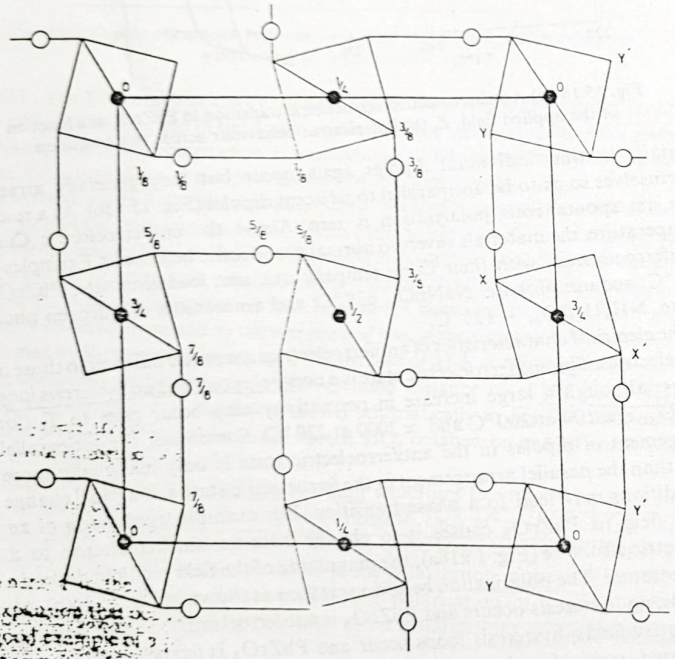
Fig. 15.16 (a) Antiferroelectric–ferroelectric transition in $PbZrO_3$ as a function of the applied field, *E*. (b) Polarization behaviour across this transition

The electrical characteristics of antiferroelectrics are rather different to those of ferroelectrics. The antiferroelectric state is a non-polar one and no hysteresis loop occurs, although a large increase in permittivity may occur close to T_c (for $PbZrO_3$, $\varepsilon' \simeq 100$ at 200 °C and $\simeq 3000$ at 230 °C). Sometimes, the antiparallel arrangement of dipoles in the antiferroelectric state is only marginally more stable than the parallel arrangement in the ferroelectric state and a small change in conditions may lead to a phase transition. For example, application of an electric field to $PbZrO_3$ causes it to change from an antiferroelectric to a ferroelectric structure (Fig. 15.16a); the magnitude of the field required depends on temperature. The polarization behaviour is then as shown in Fig. 15.16(b). At low fields, no hysteresis occurs and $PbZrO_3$ is antiferroelectric; at high positive and negative fields, hysteresis loops occur and $PbZrO_3$ is ferroelectric.

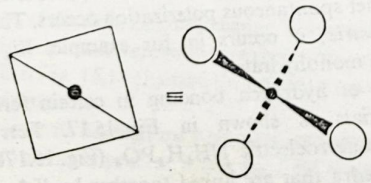
A related type of polarization phenomenon in which the structure is antiferroelectric in certain direction(s) only is shown in Fig. 15.13(c); in the *x* direction, the net polarization is zero and the structure is antiferroelectric, but in the *z* direction, a net spontaneous polarization occurs. This type of structure is known as *ferrielectric*; it occurs in, for example, $Bi_4Ti_3O_{12}$ and lithium ammonium tartate monohydrate.

The importance of hydrogen bonding in certain ferroelectric and antiferroelectric materials is shown in Fig. 15.17. Ferroelectric KH_2PO_4 (Fig. 15.17a) and antiferroelectric $NH_4H_2PO_4$ (Fig. 15.17b) are both built of isolated PO_4 tetrahedra that are linked together by K^+ and NH_4^+ ions (not shown) and hydrogen bonds. These hydrogen bonds link up oxygens in adjacent

PO_4 tetrahedra. The two structures differ mainly in the positions of hydrogen in the hydrogen bonds; both have large orthorhombic unit cells, parts of which are shown as projections down c. The PO_4 tetrahedra are seen edge-on and are represented by squares; the diagonal line in each corresponds to the upper oxygen–oxygen edge of the tetrahedron. Oxygens are therefore at the corners of the squares. The relative c heights of the tetrahedra are given by the phosphorous positions in Fig. 15.17(a); they are the same in Fig. 15.17(b). The tetrahedra are staggered along c such that the upper edge of one tetrahedron, e.g. XX', is at about the same c height as the lower edge, YY', of two adjacent tetrahedra.



(a)



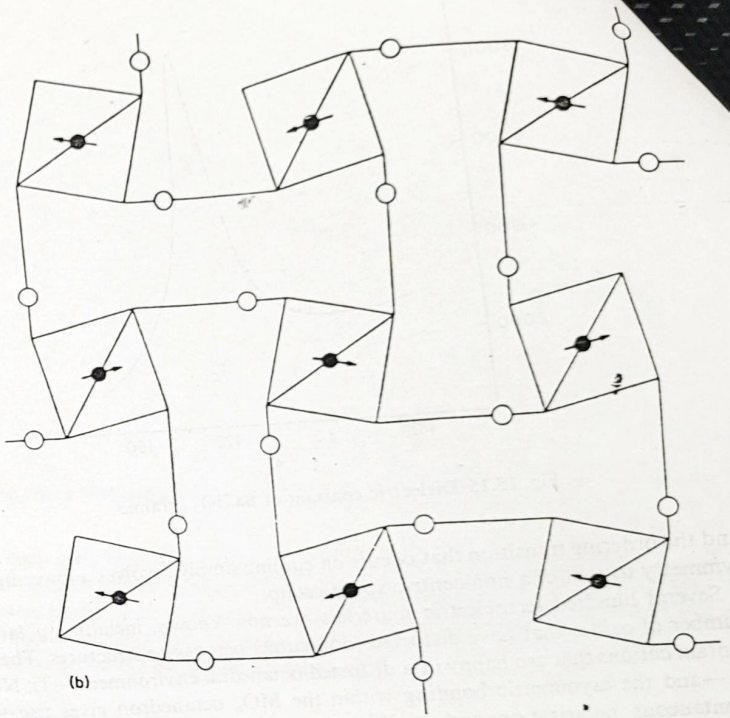


Fig. 15.17 (a) Ferroelectric KH_2PO_4 and (b) antiferroelectric $NH_4H_2PO_4$; ●POH, (001) projections

Each PO_4 tetrahedron forms four hydrogen bonds with adjacent PO_4 tetrahedra. In each of these hydrogen bonds, the hydrogens are displaced so as to be nearer to one oxygen or the other, i.e. in each hydrogen bond, the hydrogen atom has a choice of two positions, neither of which is midway along the bond. For each PO_4 tetrahedron, therefore, two hydrogens are close and two are somewhat further away. In the high temperature, paraelectric forms of KH_2PO_4 and $NH_4H_2PO_4$, the hydrogen positions are randomized over the two positions in each bond and a disordered structure obtains. In ferroelectric, low temperature, KH_2PO_4, the hydrogens order themselves so that both are associated with the upper edge of each PO_4 tetrahedron. The hydrogens are responsible indirectly for spontaneous polarization within the PO_4 tetrahedra since the phosphorus atoms are displaced downward away from the hydrogen atoms (Fig. 15.18). This generates dipoles whose directions are parallel to c. In order to reverse the directions of the dipoles it is not necessary to bodily invert the tetrahedra. Instead, a simple movement of hydrogen atoms within the H bond

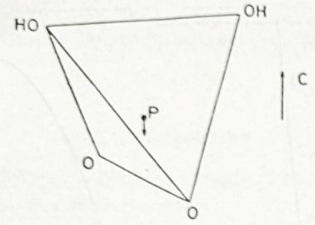


Fig. 15.18 Displacement of phosphorus within a $PO_2(OH)_2$ tetrahedron giving rise to spontaneous polarization

achieves the same effect. The two hydrogens associated with the upper oxygens in Fig. 15.17(a) move away laterally to associate themselves with the lower oxygens of adjacent tetrahedra. At the same time, two hydrogens move in to associate themselves with the lower oxygens. This motion of hydrogen atoms perpendicular to c leads to dipole reversal parallel to c.

In antiferroelectric $NH_4H_2PO_4$, the two hydrogens of each tetrahedron are associated with one upper and one lower oxygen (Fig. 15.17b): this creates dipoles in a direction perpendicular to c (i.e. in the (001) plane). The dipole directions are shown as small arrows in Fig. 15.17(b), from which it can be seen that the net polarization over the whole crystal is zero.

15.5 Pyroelectricity

Pyroelectric crystals are related to ferroelectric ones in that they are non-centrosymmetric and exhibit a net spontaneous polarization, P_s. Unlike ferroelectrics, however, the direction of P_s cannot be reversed by an applied electric field. P_s is usually temperature dependent:

$$\Delta P_s = \pi \Delta T \tag{15.18}$$

where π is the pyroelectric coefficient. This is mainly because the thermal expansion that occurs on heating changes the sizes (i.e. lengths) of the dipoles. A good example of a pyroelectric crystal is ZnO, which has the wurtzite structure. It contains a hexagonal close packed array of O^{2-} ions with Zn^{2+} ions located in one set of tetrahedral sites, say the T_+ sites (Chapter 7). The ZnO_4 tetrahedra all point in the same direction and since each tetrahedron possesses a dipole moment, the crystal has a net polarization. Opposite, (001) surfaces of a ZnO crystal must contain, respectively, Zn^{2+} and O^{2-} ions as the outermost layers of ions. Usually, however, polar impurity molecules are absorbed onto the crystal in order to neutralize the surface charges. Consequently, the pyroelectric effect in a crystal is often not detectable under constant temperature conditions but becomes apparent only when the crystal is heated, thereby changing P_s.

15.6 Piezoelectricity

Under the action of an applied mechanical stress, piezoelectric crystals polarize and develop electrical charges on opposite crystal faces. As is the case for ferro- and pyroelectricity, the crystal must belong to one of the non-centrosymmetric point groups. The occurrence of piezoelectricity depends on the crystal structure of the material and the direction of applied stress, e.g. quartz develops a polarization when subjected to a compressive stress along [100] but not when stressed along [001]. The polarization, P, and stress, σ, are related to the piezoelectric coefficient, d, by

$$P = d\sigma \tag{15.19}$$

Many crystals that contain tetrahedral groups, e.g. ZnO, ZnS, are piezoelectric since application of a shearing stress distorts the tetrahedra. One of the most important piezoelectrics is PZT, lead zirconate titanate, which is a series of solid solutions between $PbZrO_3$ and $PbTiO_3$. These solid solutions are also antiferroelectric and ferroelectric at certain compositions, as shown by a partial phase diagram (Fig. 15.19). The best piezoelectric compositions occur at $x \simeq 0.5$.

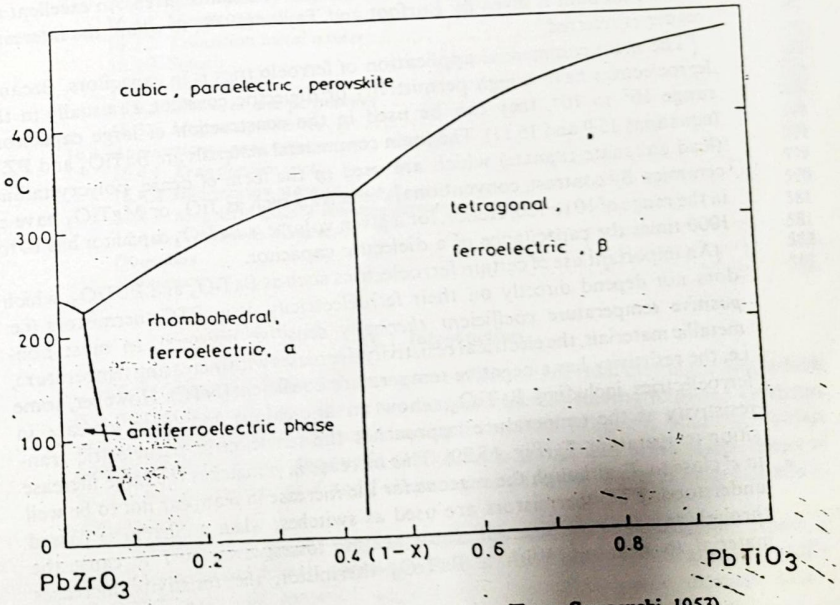


Fig. 15.19 Phase diagram for the PZT system. (From Sawaguchi, 1953)

15.7 Relationship between Ferro-, Piezo- and Pyroelectricity

All three of these properties are concerned with polar effects in crystals and, obviously, they have a great deal in common. They are related as follows. A great many materials may be included in the general class of dielectrics in which their properties, especially electrical properties, are influenced by electric fields. Piezoelectrics are a subclass of dielectrics. Piezoelectrics develop an electric charge when mechanically stressed; conversely, piezoelectrics generate mechanical stresses under the action of an applied electric field. A subclass of piezoelectrics is pyroelectrics, materials that are spontaneously polarized and therefore exhibit a net dipole moment. Some pyroelectric materials are also ferroelectric because the spontaneous polarization can be reversed under the action of an applied electric field. By definition, therefore, ferroelectric materials are also pyroelectric and piezoelectric; further, pyroelectric materials are also piezoelectric. The reverse does not hold, however; i.e. not all piezoelectric materials are pyroelectric, etc.

15.8 Applications of Ferro-, Piezo- and Pyroelectrics

Applications of these materials are considered together because they overlap considerably and, in some cases, more than one property may be involved in a particular application. Applications are very varied, especially of ferroelectrics, and only a brief summary of the less esoteric uses can be given. An excellent up-to-date account is given by Burfoot and Taylor (1979), to whom the interested reader is referred.

The main commercial application of ferroelectrics is in capacitors. Because ferroelectrics have a high permittivity or dielectric constant, ε', usually in the range 10^2 to 10^4, they can be used in the construction of large capacitors (equations 15.9 and 15.11). The main commercial materials are $BaTiO_3$ and PZT (lead zirconate titanate) which are used in the form of dense, polycrystalline ceramics. By contrast, conventional dielectrics such as TiO_2 or $MgTiO_3$ have ε' in the range of 10 to 100. Hence, for a given volume, a $BaTiO_3$ capacitor has 10 to 1000 times the capacitance of a dielectric capacitor.

An important use of certain ferroelectrics such as $BaTiO_3$ and $PbTiO_3$, which does not depend directly on their ferroelectricity, is in PTC thermistors (i.e. positive temperature coefficient *thermally sensitive resistors*). In most non-metallic materials, the electrical resistivity decreases with increasing temperature, i.e. the resistivity has a negative temperature coefficient (NTC). However, some ferroelectrics including $BaTiO_3$, show an anomalous and large increase in resistivity as the temperature approaches the ferroelectric–paraelectric transition temperature, T_c (Fig. 15.20). This increase in ρ matches the large increase in ε' close to T_c although the reasons for the increase in ρ appear not to be well understood. PTC thermistors are used as switches; when a current is passed through any resistive material, Joule heating losses, given by I^2R, cause the material to heat up. With a $BaTiO_3$ thermistor, the resistivity increases

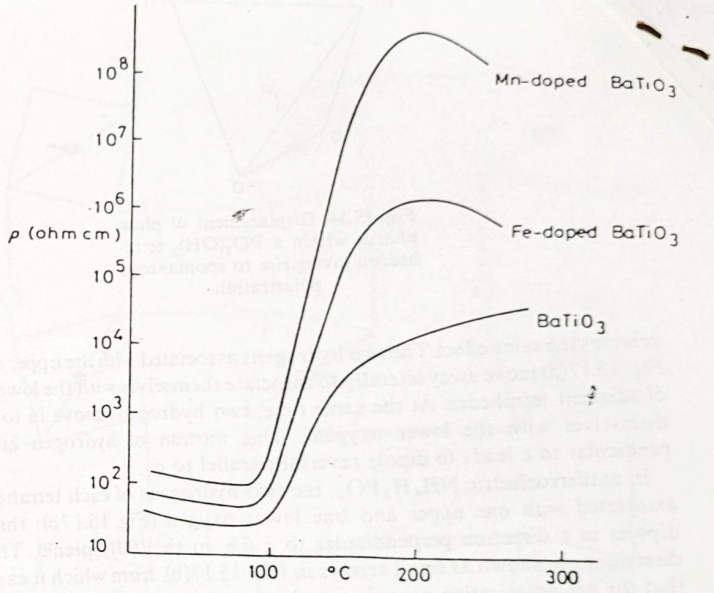


Fig. 15.20 Positive temperature coefficient resistivity in semiconducting $BaTiO_3$ ceramic with various dopants. (From Ueoka, 1974)

dramatically as it heats and consequently the current switches off. Applications include (a) thermal and current overload protection devices, in which the thermistor acts as a reusable fuse, and (b) time delay fuses. For a description of NTC thermistors based on, for example, MnO and NiO semiconductors, see Chapter 14.

Pyroelectric crystals are used mainly in infrared radiation detectors. If desired, they can be made spectrally sensitive by coating the probe surface of the crystal with appropriate absorbing material. For detectors, it is desirable to maximize the ratio π/ε', which means that ferroelectric materials with high dielectric constant are not suitable. The best detector material found to date is triglycine sulphate.

Piezoelectric crystals have been used for many years as transducers for converting mechanical to electrical energy, and vice versa. Applications are diverse, e.g. as bimorphs in microphones, earphones, loudspeakers and stereo pick-ups; as fuses, solenoid ignition systems and cigarette lighters, sonar generators and ultrasonic cleaners. More complex devices are used in transformers, filters and oscillators. Most of these applications use PZT ceramics, quartz, Rochelle salt or $Li_2SO_4 \cdot H_2O$.